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Thin Film Stabilization of Different VO₂ Polymorphs

Manish Kumar, Chirag Saharan and Sunita Rani

Abstract

In recent years, VO₂ has emerged as a popular candidate among the scientific community across the globe owing to its unique technological and fundamental aspects. VO₂ can exist in several polymorphs (such as: A, B, C, D, M₁, M₂, M₃, P, R and T) which offer a broad spectrum of functionalities suitable for numerous potential applications likewise smart windows, switching devices, memory materials, battery materials and so on. Each phase of VO₂ has specific physical and chemical properties. The device realization based on specific functionality call for stabilization of good quality single phase VO₂ thin films of desired polymorphs. Hence, the control on the growth of different VO₂ polymorphs in thin film form is very crucial. Different polymorphs of VO₂ can be stabilized by selecting the growth route, growth parameters and type of substrate etc. In this chapter, we present an overview of stabilization of the different phases of VO₂ in the thin film form and the identification of these phases mainly by X-ray diffraction and Raman spectroscopy techniques.

Keywords: thin film, VO₂, thermochromic, X-ray diffraction, Raman

1. Introduction

Thin film materials with ‘smart’ properties have attracted increasing attention in past few decades, as we move towards the smarter world [1]. This is driven by the fact that these materials react to the variation in parameters such as temperature, pressure, electric or magnetic fields etc. [2–13]. Vanadium dioxide (VO₂) is a well-known ‘smart material’ which is popular since the Morin’ work in 1959 [14]. Its monoclinic M1 phase exhibits a metal–insulator transition (MIT) near room temperature, accompanied by large changes in the structural, electronic and optical properties [15]. These distinctive features makes it attractive in smart windows, switching devices, memory materials and so on [16–18]. Being a strongly correlated electron system, VO₂ is equally attractive to condensed-matter physicists [19–22].

VO₂ can exhibit various polymorphic structures (such as: A, B, C, D, M₁, M₂, M₃, P, R and T), each having quite different physical and chemical properties [23–31]. Among these polymorphs, many are neither stable in ambient conditions nor can be easily synthesized. This happens because vanadium oxides can adopt a wide range of V:O ratios, resulting in different structural motifs. Phase space diagram (**Figure 1**) for the vanadium oxides indicates that there are more than 15 other stable vanadium oxides phases (like VO, V₂O₃, V₃O₅ etc.) and only a narrow window in phase space exist in which the pure semiconducting phase of VO₂ can be grown [32]. This narrow window strongly limits the synthesis of VO₂ either in the form of bulk crystals, thin films, or micro- and nanostructures. Nonetheless, different stoichiometric

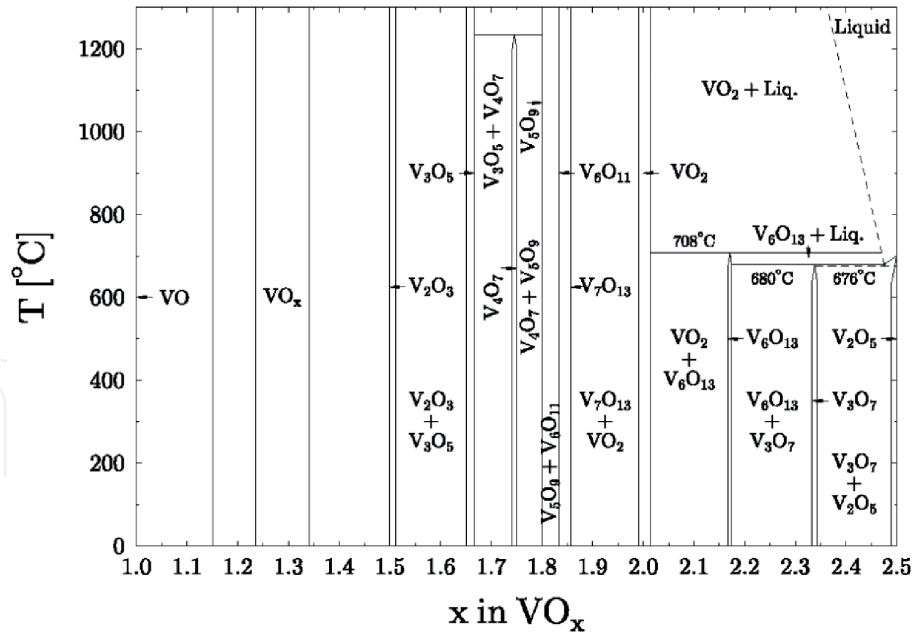


Figure 1. Phase space diagram for the vanadium oxides. Note the narrow window within which stoichiometric VO_2 can be grown for $x = 2.0$ (reprinted from Ref. [32]).

Phase	Crystal structure (space group)	Lattice parameters				Comments and References
		$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	
VO_2 (A)	Tetragonal($P4_2/\text{ncm}$) (138)	8.43	8.43	7.68		[60]
VO_2 (B)	Monoclinic(C_2/m) (12)	12.03	3.69	6.42	106.6	[60]
VO_2 (C)	Tetragonal($I4/\text{mmn}$) (139)	3.72	3.72	15.42		[24]
VO_2 (D)	Monoclinic($P2_1/c$) (13)	4.59	5.68	4.91	89.3	[26]
VO_2 (P)	Orthorhombic($P\text{bnm}$) (62)	4.95	9.33	2.89		[28]
VO_2 (M_1)	Monoclinic($P2_1/c$) (14)	5.74	4.52	5.38	122.6	[61]
VO_2 (M_2)	Monoclinic($C2/m$) (12)	9.08	5.76	4.53	91.3	[62]
VO_2 (M_3)	Monoclinic($P2_1/m$) (10)	4.50	2.89	4.61	91.7	[62]
VO_2 (T)	Triclinic($P-1$) (2)	9.06	5.77	4.52	91.4	[63]
VO_2 (R)	Tetragonal($P4_2/\text{mmn}$) (136)	4.55	4.55	2.86		[61]

Table 1. The crystallography data for VO_2 polymorphs.

VO_2 polymorphs have been stabilized using techniques such as sputtering, pulsed laser deposition (PLD), sol–gel deposition, reactive evaporation and metal–organic chemical vapor deposition (MOCVD) etc. [15, 23, 25, 31, 33–38].

Koide and Takei appears to be the first to grow VO₂ thin films by chemical vapor deposition (CVD) technique in 1967 [39]. In their deposition method, fumes of vanadium oxychloride (VOCl₃) was carried by N₂ gas into the growth chamber and was hydrolyzed on the surface of rutile substrates to give epitaxial VO₂ films. In 1967, VO₂ thin films were also grown using reactive sputtering by Fuls et al. who made the films by reactive ion-beam sputtering of a vanadium target in an argon–oxygen atmosphere [40]. PLD emerged as a deposition technique for oxide superconductors in the late 1980s, and was first used to prepare VO₂ thin films by Borek et al. in 1993 [41]. Since then, consistent efforts have been made to grow thin films of various VO₂ polymorphs by using different deposition techniques/routes. Sputtering and PLD are the leading deposition techniques used to grow different VO₂ thin films polymorphs [42–46]. This is because of the ease with which one can play the deposition parameters in these techniques to stabilize thin films of various compounds [47–60].

In this chapter we will focus on the stabilization of thin film of six main VO₂ polymorphs: VO₂ (M₁), VO₂ (M₂), VO₂ (R), VO₂ (T), VO₂ (A) and VO₂ (B). But in passing it should be noted that VO₂ polymorphs likewise VO₂ (M₃), VO₂ (P), VO₂ (C) and VO₂ (D) have also been mostly studied in bulk and nanostructure form and reports are missing on thin film stabilization of these phases [24–29, 31]. Space group and lattice parameters of different VO₂ polymorphs known to us are tabulated in **Table 1**.

2. Thin film growth of different VO₂ polymorphs

2.1 VO₂ (M₁) and VO₂ (R) phase thin films

Monoclinic VO₂ (M₁) ($a = 5.74 \text{ \AA}$, $b = 4.52 \text{ \AA}$, $c = 5.38 \text{ \AA}$, $\beta = 122.6^\circ$) with space group P2₁/c is the most widely studied inorganic thermochromic material which is an insulator at room temperature. It shows a first-order MIT at 68°C with a concomitant structural transition into rutile tetragonal VO₂ (R) ($a = b = 4.55 \text{ \AA}$, $c = 2.86 \text{ \AA}$) having space group P4₂/mmn [61]. Because of MIT and the associated huge changes in the structural, electronic and optical properties, VO₂ (M₁) and VO₂ (R) are attractive for applications in smart windows, switching devices, memory materials and so on [16, 17].

Figure 2 shows the structural arrangement of four different phases of VO₂ [64]. In the VO₂ (R) phase, the vanadium atoms are equally spaced along the rutile c axis (c_R), while in the VO₂ (M₁) phase, simultaneous dimerization and tilting in equivalent chains occur, leading to a zigzag pattern.

Highly oriented VO₂ (M₁) thin films on R-cut sapphire substrate were prepared by Borek et al. using PLD [41]. They ablated metallic vanadium target by a KrF pulsed excimer laser in an ultrahigh vacuum deposition chamber with Ar and O₂ (10:1) atmosphere of 100–200 mTorr, and a substrate temperature (T_s) $\sim 500^\circ\text{C}$ followed by 1 hour post deposition annealing in the same environment. Since then PLD was employed by number of groups to grow good quality VO₂ (M₁) thin films by varying the deposition parameters and post deposition treatment [44–46, 65]. Several other techniques such as sputtering, CVD, etc. were also employed to grow polycrystalline and epitaxial VO₂ (M₁) thin films on various substrates of different orientation [34, 42, 43, 66–69]. To date, most VO₂ (M₁) films have been grown on substrates such as sapphire (c-type, m-type, r-type and a-type), TiO₂, perovskite oxides, Si and Quartz. **Figure 3(a)** shows the grazing incidence X-ray diffraction (GIXRD) data of polycrystalline VO₂ (M₁) thin film by Kumar et al. which was

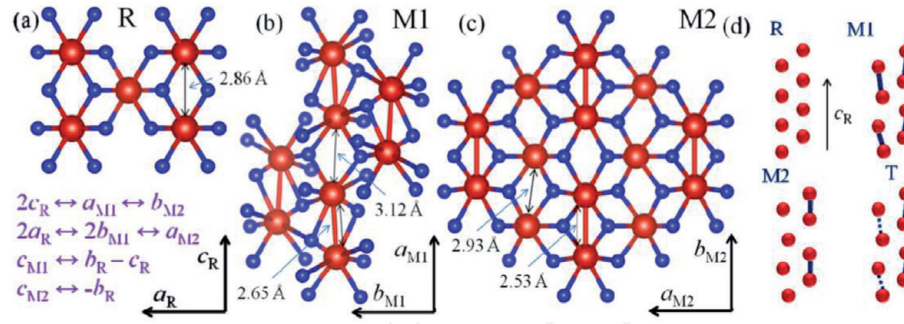


Figure 2.

The schematic structures for (a) rutile (R), (b) monoclinic M₁, and (c) M₂ phases of VO₂. Red and blue balls denote vanadium and oxygen atoms, respectively. (d) The arrangement of vanadium chains in the four phases without oxygen atoms (a-d reprinted from Ref. [64]).

grown on quartz substrate by sputtering VO₂ at room temperature and post deposition annealing at 500°C [69]. **Figure 3(b)–d** depict the X-ray diffraction (XRD) patterns of VO₂ (M₁) thin film grown on TiO₂ and Al₂O₃ substrates of different orientation [46, 70].

VO₂ (R) is the high temperature phase of VO₂ (M₁). So, VO₂ (M₁) thin films generally transforms to VO₂ (R) phase when heated above the MIT temperature. Apart from this, thin films showing VO₂ (R) phase at room temperature can also be stabilized by strain, hydrogenation, oxygen vacancies and doping etc. [71–76]. Fan et al. reported the growth of ultrathin VO₂ (R) phase thin film on TiO₂ (002) substrate [71]. Y. Zhao et al. showed that hydrogenation can also lead to growth of VO₂ (R) phase thin film [72]. Very recently, Liang et al. described that increase in concentration of W dopant in V_{1-x}W_xO₂/Si thin films favors the growth of VO₂ (R) phase [73]. **Figure 4** shows the XRD patterns of VO₂ (R) phase thin films grown by different groups.

2.2 VO₂ (T) phase and VO₂ (M₂) phase thin films

VO₂ (T) phase and VO₂ (M₂) are known to be Mott-Hubbard type insulator which may find use in Motttronics and novel electronic transport applications [15, 18]. These phases are structurally different from VO₂ (M₁) and VO₂ (R) phase because of dissimilar types of vanadium chains and dimerization as shown in **Figure 2**. VO₂ (M₂) phase contains two distinct types of vanadium chains: one half of the vanadium atoms pair but do not tilt, while the other half are equidistant which tilts but do not pair. Triclinic phase i.e. VO₂ (T) phase can be thought of as an intermediate phase between VO₂ (M₁) and VO₂ (M₂) phases, having two types of inequivalent vanadium chains (or sublattices) in which the vanadium atoms are paired and tilted to different degrees. VO₂ (T) phase and VO₂ (M₂) are not as stable phase as VO₂ (M₁) and VO₂ (R). But, doping and/or strain can stabilize these phases [15, 35, 77]. Strelcov et al. presented a phase diagram which demonstrate the influence of chemical doping and uniaxial stress on the phase structure of VO₂ [35]. This phase diagram (**Figure 5(a)**) indicates that either of M₁, M₂, T, or R phase of VO₂ can exist depending on the type of dopant and/or stress. Majid et al. reported the Cr doping driven growth of VO₂ (T) phase thin films [15]. **Figure 5(b)** shows their XRD pattern of grown VO₂ (M₁) and VO₂ (T) phase thin films. Stress-induced VO₂ films with M₂ monoclinic phase stable at room temperature; were grown by Okimura et al. using inductively coupled plasma-assisted (ICP) reactive sputtering technique with various rf power fed to the coil for ICP (**Figure 5(c)**) at constant Ts of 450°C and at varying Ts, under constant rf power (**Figure 5(d)**) [77]. Apart from this work, there are not much reports on the growth of single phase VO₂ (M₂) thin films which are stable at room temperature. But, there are numerous reports on the evolution of intermediate M₂ phase in VO₂ thin films

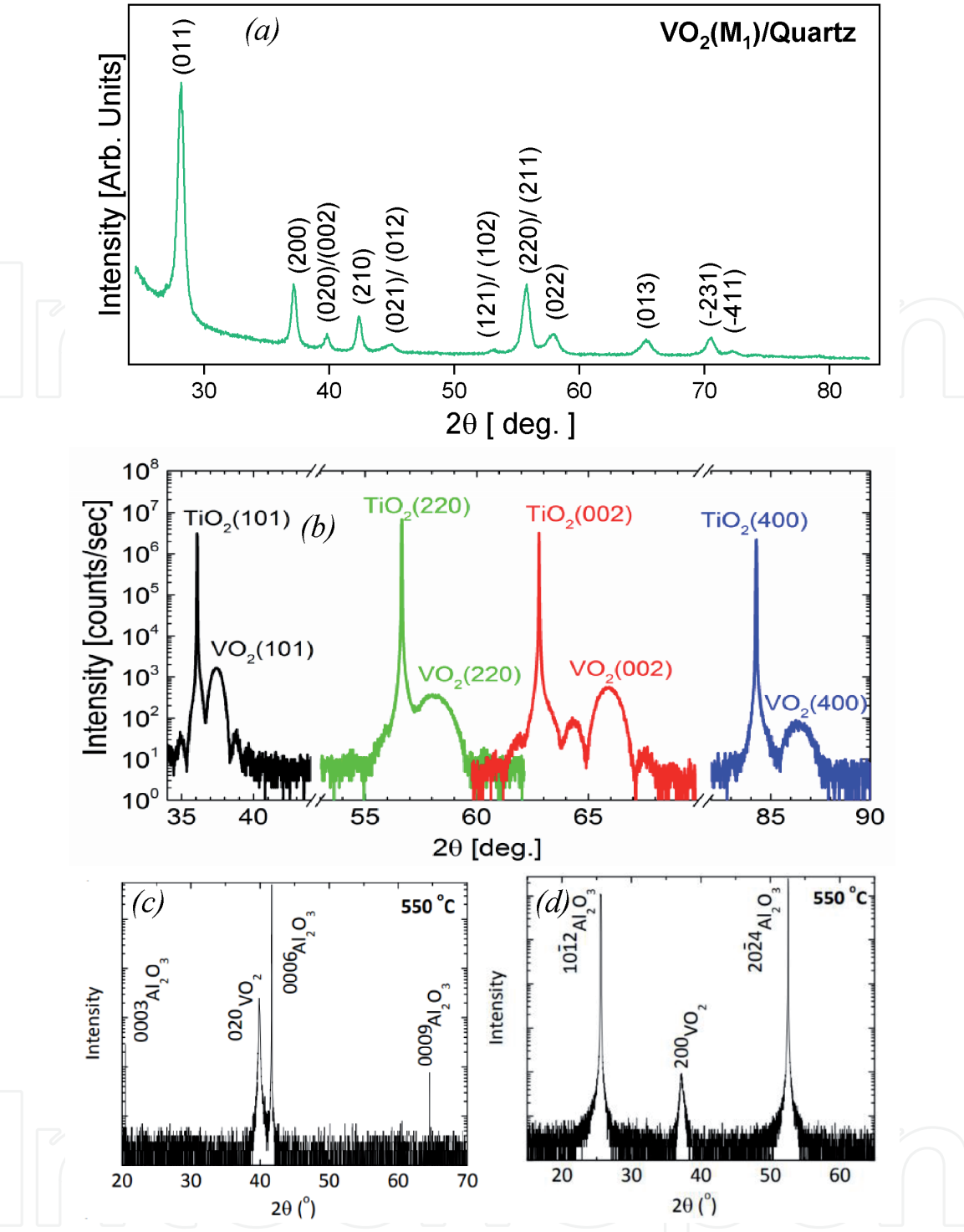


Figure 3. (a) GIXRD data of VO₂ (M₁) thin film prepared on quartz substrate [69]. XRD data of epitaxial VO₂ (M₁) thin films grown on (b) TiO₂ substrates of different orientation (reprinted from Ref. [46]), (c) c-cut sapphire and (d) r-cut sapphire (c, d adopted from Ref. [70]).

during the monoclinic M₁ to rutile R transition [15, 69, 78–81]. This intermediate M₂ phase in VO₂ thin film can be introduced by selecting the particular substrate temperature, doping, thickness etc. Kumar et al. witnessed the intermediate M₂ phase temperature dependent XRD measurements across the MIT transition in polycrystalline VO₂ thin films grown on quartz substrate using sputtering technique followed by rapid thermal annealing at 530°C (**Figure 6(b)**) [69]. However, they have not observed the intermediate M₂ phase for films annealed at 500°C (**Figure 6(a)**). Majid et al. noticed the evolution of intermediate M₂ phase in temperature dependent Raman measurements of Cr doped VO₂ thin films during T → R phase transition (**Figure 6(d)**) [15]. For undoped VO₂ thin films normal M₁→R phase transition crossover was observed

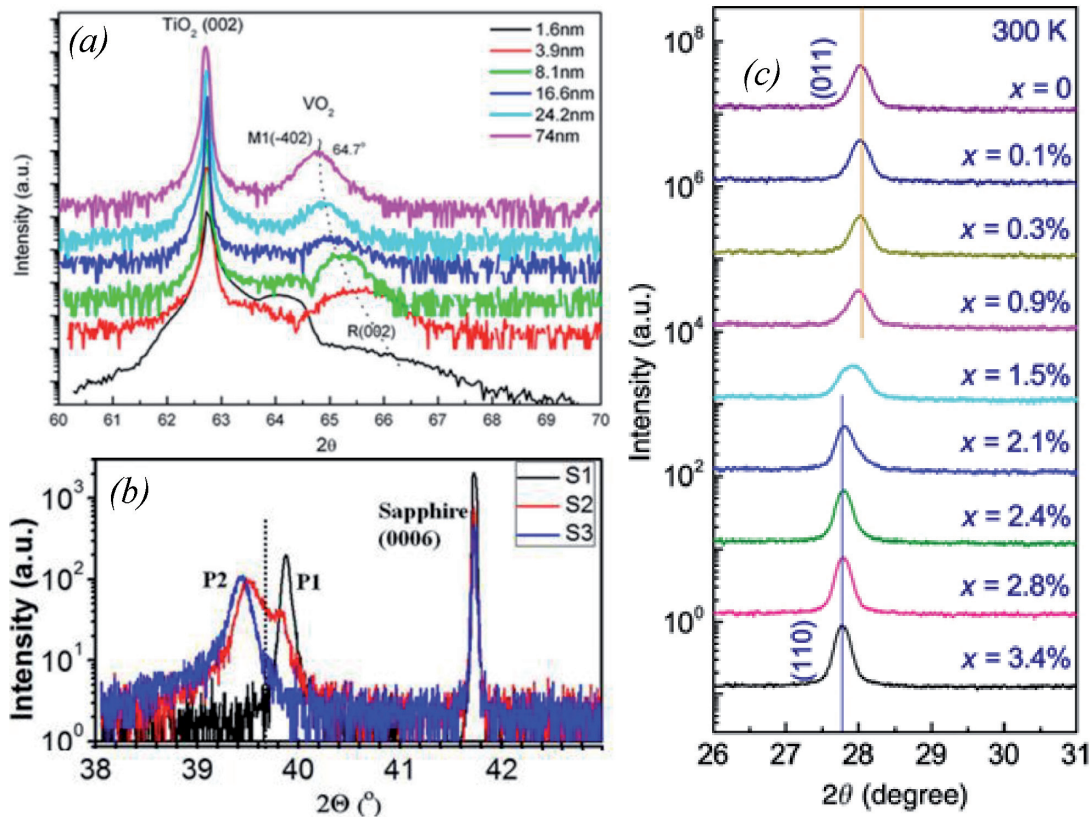


Figure 4.

(a) XRD profiles for thickness-dependence VO_2 films on TiO_2 substrate [Reprinted with permission from Fan et al [71]. Copyright (2014) American Chemical Society]. (b) XRD of pure (M_1 phase) and hydrogen-doping stabilized metallic (R phase) VO_2 thin films prepared on sapphire substrate (Reprinted from Ref. [72], with the permission of AIP Publishing). (c) Room temperature XRD of different $\text{V}_{1-x}\text{W}_x\text{O}_2/\text{Si}$ thin films (adopted from Ref. [73]).

without signatures of intermediate M_2 phase °C (**Figure 6(c)**). Ji et al. stressed the role of microstructure on the M_1 - M_2 phase transition in epitaxial VO_2 thin films of different thicknesses [78]. Their temperature dependent Raman measurement result on 90 nm and 150 nm thick VO_2 thin film sample are depicted in **Figure 6(e)** and **(f)** respectively. Azhan et al. also found intermediate M_2 phase in VO_2 thin films with large crystalline domains [79].

2.3 VO_2 (A) and VO_2 (B) phase thin films

The layered polymorphs VO_2 (A) and VO_2 (B) are important materials from science and technology perspective. VO_2 (B) has been long considered as a promising electrode material for Li ion batteries since the after report of Li et al. in 1994 [82]. It emerged as a promising cathode material owing to its layered structure and outstanding electro-chemical performance [83, 84]. Also, it is important for the study of strong electronic correlations resulting from structure. On the other hand, VO_2 (A) phase is highly metastable and therefore the physical properties and the potential for technical applications have not been explored in detail. This phase is an intermediate phase between VO_2 (B) and VO_2 (R), and has a reversible phase transition at $\sim 162^\circ\text{C}$ [85, 86]. The crystal structure of VO_2 (A) and VO_2 (B) phase with possible epitaxial relation on SrTiO_3 substrate, are illustrated in **Figure 7(a)** and **(b)** respectively [23]. At room temperature, the metastable monoclinic VO_2 (B) adopts a structure derived from V_2O_5 and belongs to space group C2/m while VO_2 (A) adopts a tetragonal unit cell with a space group $\text{P4}_2/\text{ncm}$ [23]. Growth of single crystalline VO_2 (B) is very challenging due to the complex crystal structure. Similarly to VO_2 (B), the study of VO_2 (A) has so far been limited.

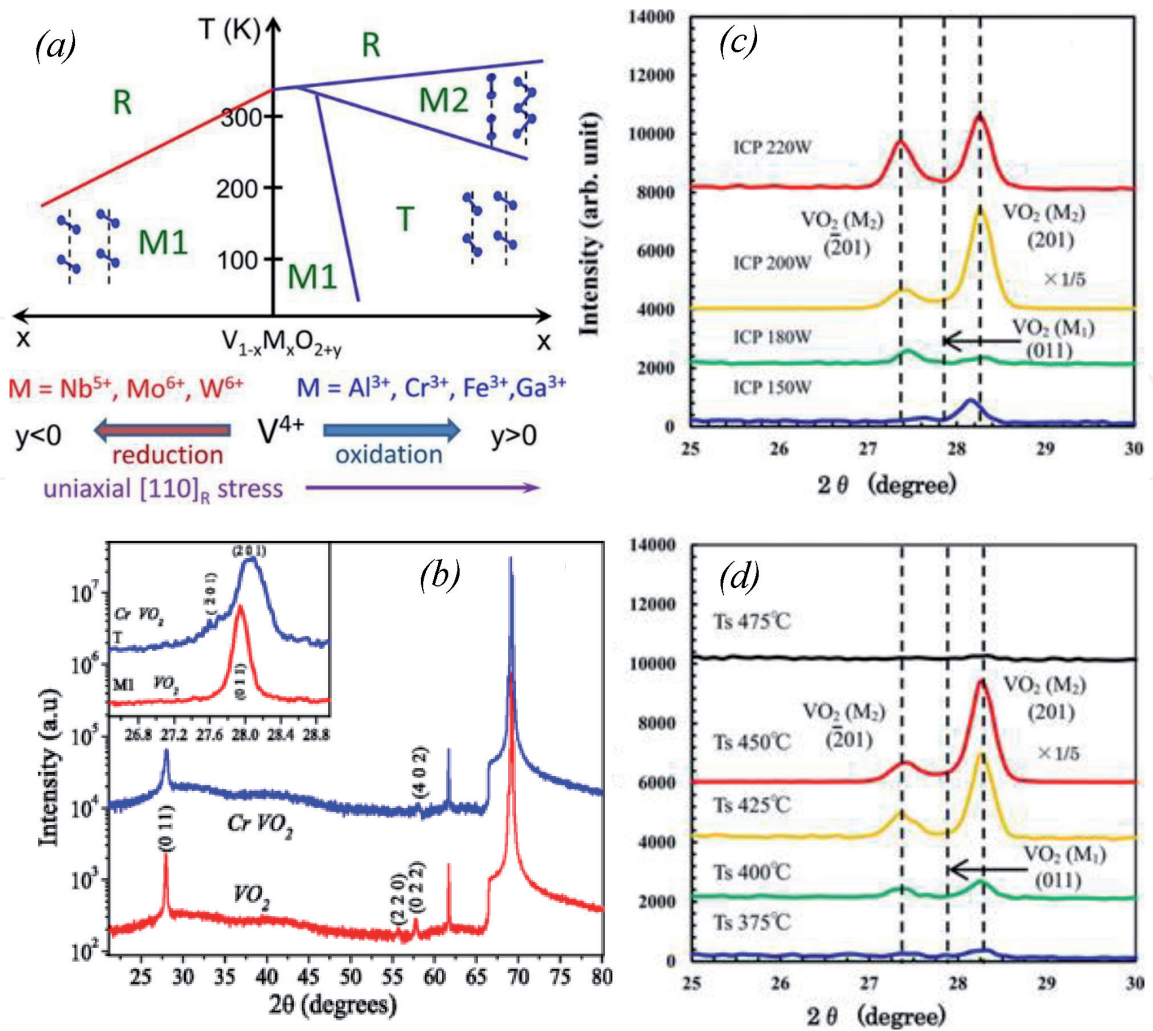


Figure 5.
(a) A temperature-composition phase diagram of VO₂, demonstrating the influence of chemical doping and uniaxial stress on the phase structure of VO₂ (reprinted with permission from Strelcov et al. [35]. Copyright 2012 American Chemical Society). (b), room-temperature XRD patterns of the pure (M₁ phase) and Cr-doped (T phase) VO₂ thin films on the [001] Si substrate (adapted from Ref. [15]). (c and d) XRD patterns of the VO₂ films grown on quartz substrates with various RF power fed to the coil for ICP, at constant Ts of 450°C and at varying Ts, under constant RF power (Reprinted from Ref. [77], with the permission of AIP Publishing).

Recently; several reports are focused on VO₂ (A) and VO₂ (B) phases in the form of bulk and nano-powders where annealing treatment causes them to revert to stable VO₂ (M₁) phase [25]. Chen et al. appears to be the first to report the growth of textured VO₂ (B) films with thickness only <25 nm on SrTiO₃ (001) substrate [87].

The good matching of the a – b plane of VO₂ (B) to that of (001)-oriented perovskites enables the epitaxial growth of phase-pure VO₂ (B) thin films on perovskite substrates, such as SrTiO₃ and LaAlO₃. Srivastava et al. successfully stabilized the single phase VO₂ (B) and VO₂ (A) thin films by tuning the laser rotation rate and oxygen partial pressure during PLD while keeping the constant substrate temperature ($T_s = 500^\circ\text{C}$) [23]. The XRD pattern of their grown films and the phase diagram of used deposition parameters are shown in **Figure 7(c)** and **(d)** respectively. Lee et al. argued that a proper choice of T_s is critical among the deposition parameters for the growth of VO₂ (A) and VO₂ (B) phase thin film on perovskite substrates [60]. They found that the thin films of these phases can reproducibly grow at T_s lower than 430°C only (**Figure 8(a)** and **(b)**). Moreover, VO₂ (A) phase can also appear as an intermediate phase (**Figure 8(c)**) when annealing is carried out for VO₂ (B) → VO₂ (R) conversion [60]. Wong et al. successfully synthesize thin

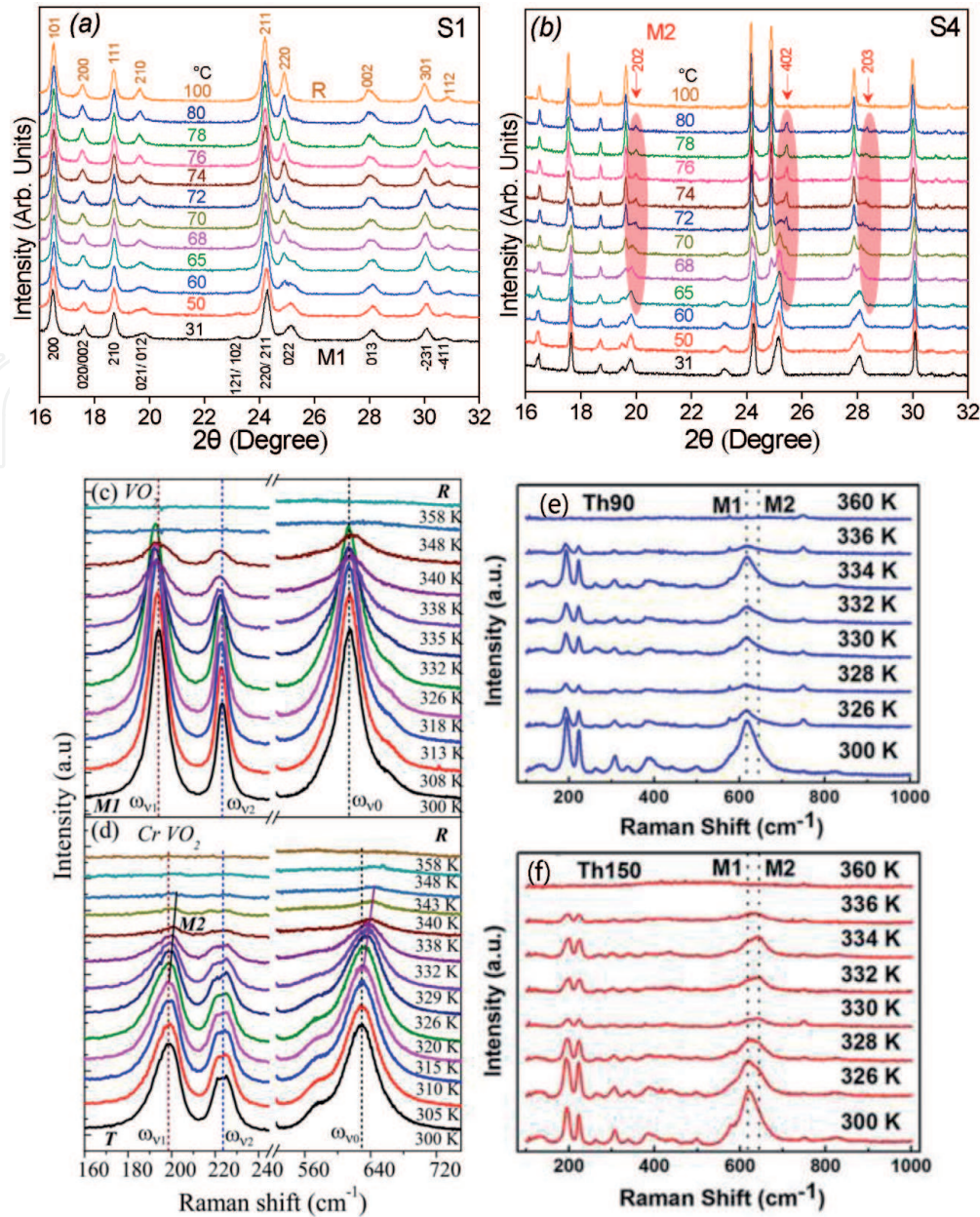


Figure 6.

Temperature dependence of XRD data (at X-ray wavelength (λ) = 0.0693 nm) during heating cycle for VO₂ thin film annealed at (a) 500°C and (b) 530°C (a,b adopted from Ref. [69]). Temperature-dependent Raman spectra of (c) pure and (d) Cr-doped VO₂ thin films collected in the cooling cycles (c, d adopted from Ref. [15]). Temperature dependent Raman spectra of (e) 90 nm and (f) 150 nm thick VO₂ thin film grown on Al₂O₃ substrate (e, f adopted from Ref. [78]).

films of the metastable VO₂ (B) polymorph on (001) LaAlO₃ at deposition temperature $T_s = 325^\circ\text{C}$ (**Figure 8(d)**) [70]. Very recently, Choi et al. grown epitaxial VO₂ (A) and VO₂ (B) thin films having tungsten doping were grown on (011)-oriented SrTiO₃ and 001)-oriented LaAlO₃ substrate respectively using PLD [88].

3. Conclusions

An overview of thin film stabilization of different VO₂ polymorphs i.e. VO₂ (M₁), VO₂ (M₂), VO₂ (R), VO₂ (T), VO₂ (A) and VO₂ (B) is presented in this chapter. It is understood that one can stabilize the thin film of a particular VO₂ polymorph by properly selecting the deposition technique, growth parameters, type of substrate and dopant etc.

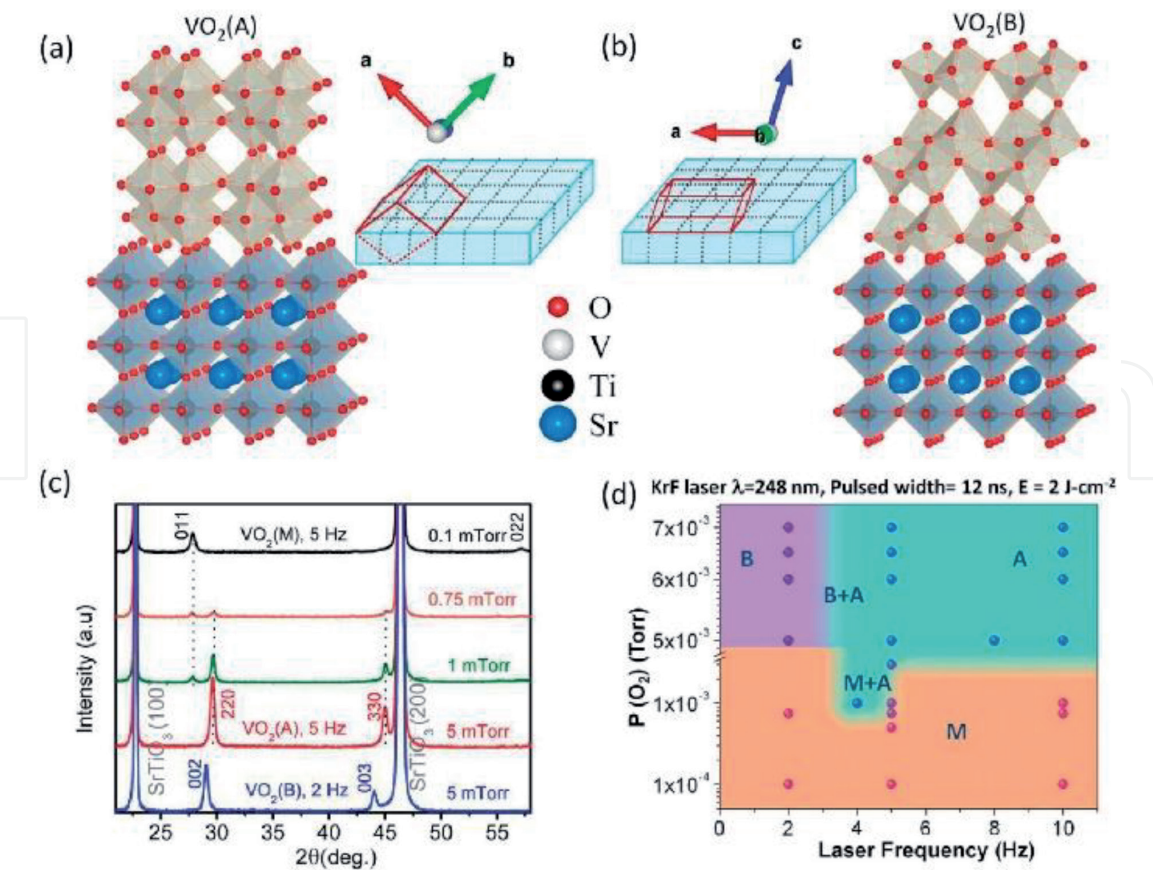


Figure 7.
The schematic crystal structure representation of (a) 220 orientated VO₂ (A), (b) 002 orientated VO₂ (B) grown on SrTiO₃ (100) substrate. (c) XRD patterns showing different phases for VO₂ thin films grown at various deposition parameters. (d) Phase diagram showing the role of laser frequency and oxygen pressure during pulsed laser deposition for different polymorphs of VO₂ thin films (a-d adopted from Ref. [23]).

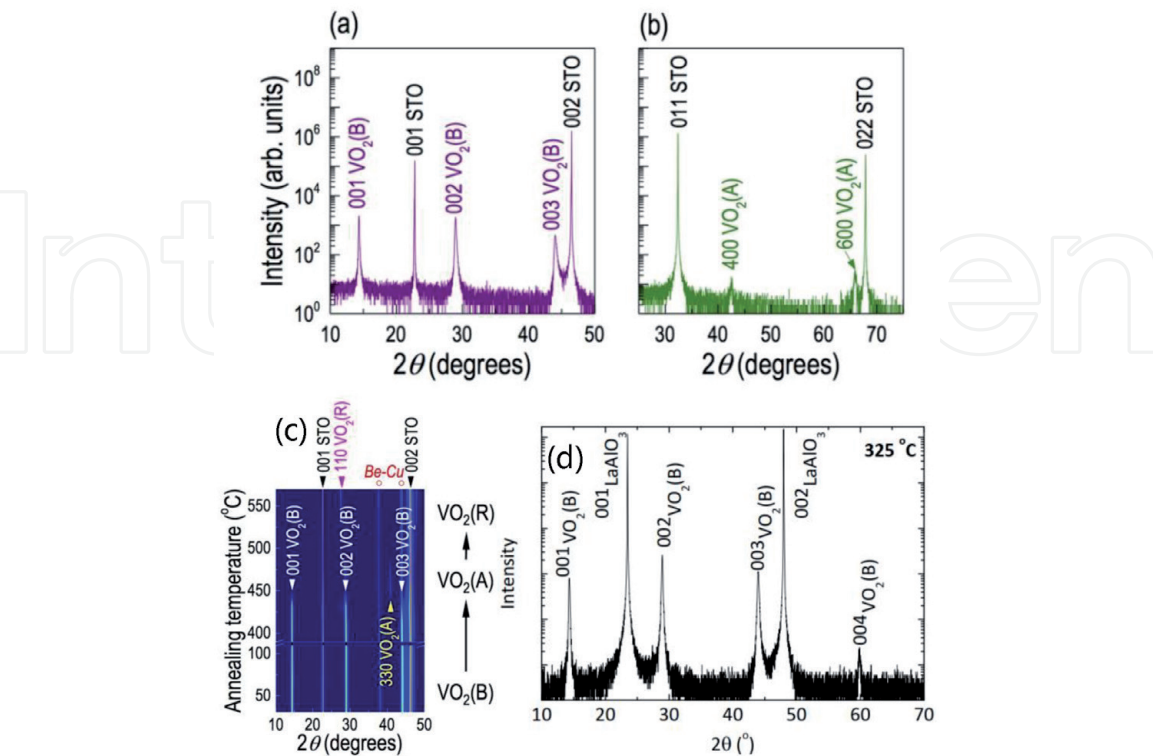


Figure 8.
XRD patterns of (a) VO₂ (B) and (b) VO₂ (A) thin film on SrTiO₃ (001) and (011) substrates respectively. (c) XRD during annealing of VO₂ (B)/STO sample (a-c adopted from Ref. [60]). (d) XRD scan of VO₂ (B) film grown on LaAlO₃ (001) substrate (adopted from Ref. [70]).

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Conflict of interest

The authors declare no conflict of interest.

Notes/thanks/other declarations

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References

- [1] Shahinpoor M, editor. Fundamentals of Smart Materials. 1st ed. Cambridge; Royal Society of Chemistry; 2020.338 p. ISBN: 9781782626459
- [2] Kumar M, Phase DM, Choudhary RJ, Lee HH. Structure and functionalities of manganite/cuprate thin film. *Current Applied Physics*. 2018;**18S**:33-36. DOI: 10.1016/j.cap.2017.11.009
- [3] Kumar M, Choudhary RJ, Shukla DK, Phase DM. Metastable magnetic state and magnetotransport in disordered manganite thin film. *Journal of Applied Physics*. 2014;**115**:163904. DOI: 10.1063/1.4873300
- [4] Dagotto E. Complexity in strongly correlated electronic systems. *Science*. 2005;**309**:257. DOI: 10.1126/science.1107559
- [5] Kumar M, Choudhary RJ, Phase DM. Valence band structure of YMnO₃ and the spin orbit coupling. *Applied Physics Letters*. 2013;**102**:182902. DOI: 10.1063/1.4804618
- [6] Kumar M, Choudhary RJ, Phase DM. Magnetic and electronic properties of La_{0.7}Ca_{0.3}MnO₃/h-YMnO₃ bilayer. *Journal of Vacuum Science and Technology A*. 2016;**34**:021506. DOI: 10.1116/1.4937356
- [7] Panchal G, Choudhary RJ, Kumar M, Phase DM. Interfacial spin glass mediated spontaneous exchange bias effect in self-assembled La_{0.7}Sr_{0.3}MnO₃: NiO nanocomposite thin films. *J. Alloy. Compd*. 2019;**796**:196-202. DOI: 10.1016/j.jallcom.2019.05.033
- [8] Kumar M, Phase DM, Choudhary RJ. Structural, ferroelectric and dielectric properties of multiferroic YMnO₃ synthesized via microwave assisted radiant hybrid sintering. *Heliyon*. 2019;**4**:e01691. DOI: 10.1016/j.heliyon.2019.e01691
- [9] Kumar M, Phase DM, Choudhary RJ, Upadhyay SK, Reddy VR. Microwave assisted radiant hybrid sintering of YMnO₃ ceramic: Reduction of microcracking and leakage current. *Ceramics International*. 2018;**44**:8196. DOI: 10.1016/j.ceramint.2018.01.268
- [10] Kumar M, Choudhary RJ, Phase DM. Metastable magnetic state and exchange bias training effect in Mn-rich YMnO₃ thin films. *Journal of Physics D: Applied Physics*. 2015;**48**:125003. DOI: 10.1088/0022-3727/48/12/125003
- [11] Kumar M, Choudhary RJ, Shukla DK, Phase DM. Superspin glassy behaviour of La_{0.7}Ca_{0.3}Mn_{0.85}Al_{0.15}O₃ thin film. *Journal of Applied Physics*. 2014;**116**:033917. DOI: 10.1063/1.4890507
- [12] Kumar M, Choudhary RJ, Phase DM. Structural and multiferroic properties of self-doped yttrium manganites YMn_{1-x}O₃. *AIP Conf. Proc*. 2015;**1661**:07005. DOI: 10.1063/1.4915383
- [13] Devi V, Kumar M, Wadikar AD, Choudhary RJ, Phase DM, Joshi BC. Electronic and multiferroic properties of Zn_{0.85}Mg_{0.15}O thin film. *AIP Conf. Proc*. 2015;**1665**:080065. DOI: 10.1063/1.4917969
- [14] Morin FJ. Oxides which show a metal-to-insulator transition at the neel temperature. *Physical Review Letters*. 1959;**3**:34. DOI: 10.1103/PhysRevLett.3.34
- [15] Majid SS, Shukla DK, Rahman F, Khan S, Gautam K, Ahad A, et al. Insulator-metal transitions in the T phase Cr doped and M1 phase undoped VO₂ thin films. *Physical Review B*. 2018;**98**:075152. DOI: 10.1103/PhysRevB.98.075152

- [16] Liu K, Lee S, Yang S, Delaire O, Wu J. Recent progresses on physics and applications of vanadium dioxide. *Materials Today*. 2018;**21**:875. DOI: 10.1016/j.mattod.2018.03.029
- [17] Yang Z, Ko C, Ramanathan S. Oxide electronics utilizing ultrafast metal-insulator transitions. *Annual Review of Materials Research*. 2011;**41**:337. DOI: 10.1146/annurev-matsci-062910-100347
- [18] Zhou Y, Ramanathan S. Mott memory and neuromorphic devices. *Proceedings of the IEEE*. 2015;**103**:1289. DOI: 10.1109/jproc.2015.2431914
- [19] Shao Z, Cao X, Luo H, Jin P. Recent progress in the phase-transition mechanism and modulation of vanadium dioxide materials. *NPG Asia Materials*. 2018;**10**:581. DOI: 10.1038/s41427-018-0061-2
- [20] Haverkort MW, Hu Z, Tanaka A, Reichelt W, Streltsov SV, Korotin MA, et al. Orbital-assisted metal-insulator transition in VO₂. *Physical Review Letters*. 2015;**95**:196404. DOI: 10.1103/PhysRevLett.95.196404
- [21] O'Callahan BT, Jones AC, Park JH, Cobden DH, Atkin JM, Raschke MB. Inhomogeneity of the ultrafast insulator-to-metal transition dynamics of VO₂. *Nature Communications*. 2015;**6**:6849. DOI: 10.1038/ncomms7849
- [22] Gray AX, Jeong J, Aetukuri NP, Granitzka Chen PZ, Kukreja R, Higley D, et al. Correlation-driven insulator-metal transition in near-ideal vanadium dioxide films. *Physical Review Letters*. 2016;**116**:1. DOI: 10.1103/PhysRevLett.116.116403
- [23] Srivastava A, Rotella H, Saha S, Pal B, Kalon G, Mathew S, et al. Selective growth of single phase VO₂(A, B, and M) polymorph thin films. *APL Materials*. 2015;**3**:026101. DOI: 10.1063/1.4906880
- [24] Hagrman D, Zubietta J, Warren CJ, Linda MM, Michael MJT, Robert CH. A new polymorph of VO₂ prepared by soft chemical methods. *Journal of Solid State Chemistry*. 1998;**138**:178. DOI: 10.1006/jssc.1997.7575
- [25] Li M, Magdassi S, Gao Y, Long Y. Hydrothermal synthesis of VO₂ polymorphs: Advantages, challenges and prospects for the application of energy efficient smart windows. *Small*. 2017;**13**:1701147. DOI: 10.1002/sml.201701147
- [26] Liu L, Cao F, Yao T, Xu Y, Zhou M, Qu B, et al. New-phase VO₂ micro/nanostructures: Investigation of phase transformation and magnetic property. *New Journal of Chemistry*. 2012;**36**:619. DOI: 10.1039/c1nj20798a
- [27] Song ZD, Zhang LM, Xia F, Webster N, Song J, Liu B, et al. Controllable synthesis of VO₂(D) and their conversion to VO₂(M) nanostructures with thermochromic phase transition properties. *Inorganic Chemistry Frontiers*. 2016;**3**:1035. DOI: 10.1039/C6QI00102E
- [28] Wu C, Hu Z, Wang W, Zhang M, Yang J, Xie Y. Synthetic paramontroseite VO₂ with good aqueous lithium-ion battery performance. *Chemical Communications*. 2008;**(33)**:3891. DOI: 10.1039/B806009F
- [29] Braham E, Andrews JL, Alivio TEG, Flier NA, Banerjee S. Stabilization of a metastable tunnel-structured orthorhombic phase of VO₂ upon iridium doping. *Phys. Status Solidi A-Appl. Mat*. 2018;**215**:1700884. DOI: 10.1002/pssa.201700884
- [30] Park JH, Coy JM, Kasirga TS, Huang C, Fei Z, Hunter S, et al. Measurement of a solid-state triple point at the metal-insulator transition in VO₂. *Nature*. 2013;**500**:431. DOI: 10.1038/nature12425

- [31] Galy J, Miehle G. Ab initio structures of (M2) and (M3) VO₂ high pressure phases. *Solid State Sciences*. 1999;**1**:433. DOI: 10.1016/S1293-2558(00)80096-5
- [32] Katzke H, Toledano P, Depmeier W. *Physical Review B*. 2003;**68**:024109. DOI: 10.1103/PhysRevB.68.024109
- [33] MacChesney JB, Potter JF, Guggenheim HJ. Preparation and properties of vanadium dioxide films. *Journal of the Electrochemical Society*. 1968;**115**:52. DOI: 10.1149/1.2411002
- [34] Kumar M, Singh JP, Chae KW, Park J, Lee HH. Annealing effect on phase transition and thermochromic properties of VO₂ thin films. *Superlattices and Microstructures*. 2020;**137**:106335. DOI: 10.1016/j.spmi.2019.106335
- [35] Strelcov E, Tselev A, Ivanov I, Budai JD, Zhang J, Tischler JZ, et al. Doping-based stabilization of the M2 phase in free-standing VO₂ nanostructures at room temperature. *Nano Letters*. 2012;**12**:6198. DOI: 10.1021/nl303065h
- [36] Sahana MB, Dharmaprakash MS, Shivashankar SA. Microstructure and properties of VO₂ thin films deposited by MOCVD from vanadyl acetylacetonate. *Journal of Materials Chemistry*. 2002;**12**:333. DOI: 10.1039/b106563g
- [37] Warwick MEA, Binions R. Chemical vapour deposition of thermochromic vanadium dioxide thin films for energy efficient glazing. *Journal of Solid State Chemistry*. 2014;**214**:53. DOI: 10.1016/j.jssc.2013.10.040
- [38] Seyfour MM, Binions R. Sol-gel approaches to thermochromic vanadium dioxide coating for smart glazing application. *Solar Energy Materials & Solar Cells*. 2017;**159**:52. DOI: 10.1016/j.solmat.2016.08.035
- [39] Koide S, Takei H. Epitaxial growth of VO₂ single crystals and their anisotropic properties in electrical resistivities. *Journal of the Physical Society of Japan*. 1967;**22**:946. DOI: 10.1143/JPSJ.22.946
- [40] Fuls EN, Hensler DH, Ross AR. Reactively sputtered vanadium dioxide thin films. *Applied Physics Letters*. 1967;**10**:199. DOI: 10.1063/1.1754909
- [41] Borek M, Qian F, Nagabushnam V, Singh RK. Pulsed-laser deposition of oriented VO₂ thin films on R-cut sapphire substrates. *Applied Physics Letters*. 1993;**63**:3288. DOI: 10.1063/1.110177
- [42] Manish K, Rani S, Lee HH. Thermochromic VO₂ thin films: Growth and characterization. *AIP Conf. Proc.* 2019;**2142**:080007. DOI: 10.1063/1.5122435
- [43] Kumar M, Rani S, Lee HH. Effect of Ti:ZnO layer on the phase transition and optical properties of VO₂ film. *Journal of the Korean Physical Society*. 2019;**75**:519-522. DOI: 10.3938/jkps.75.519
- [44] Kim DH, Kwok HS. Pulsed laser deposition of VO₂ thin films. *Applied Physics Letters*. 1994;**65**:3188. DOI: 10.1063/1.112476
- [45] Émond N, Hendaoui A, Ibrahim A, Al-Naib I, Ozaki T, Chaker M. Transmission of reactive pulsed laser deposited VO₂ films in the THz domain. *Applied Surface Science*. 2016;**379**:377. DOI: 10.1016/j.apsusc.2016.04.018
- [46] Jeong J, Aetukuri NB, Passarello D, Conradson SD, Samant MG, Parkin. Giant reversible, facet-dependent, structural changes in a correlated-electron insulator induced by ionic liquid gating. *SSP. PNAS*. 2015;**112**:1013. DOI: 10.1073/pnas.1419051112

- [47] Kumar M, Choudhary RJ, Phase DM. Growth of different phases of yttrium manganese oxide thin films by pulsed laser deposition. *AIP Conf. Proc.* 2012;**1447**:655. DOI: 10.1063/1.4710173
- [48] Devi V, Joshi BC, Kumar M, Choudhary RJ. Structural and optical properties of Cd and Mg doped zinc oxide thin films deposited by pulsed laser deposition. *Journal of Physics: Conference Series.* 2014;**534**:012047. DOI: 10.1088/1742-6596/534/1/012047
- [49] Devi V, Kumar M, Kumar R, Joshi BC. Effect of substrate temperature and oxygen partial pressure on structural and optical properties of Mg doped ZnO thin films. *Ceramics International.* 2015;**41**:6269. DOI: 10.1016/j.ceramint.2015.01.049
- [50] Devi V, Kumar M, Shukla DK, Choudhary RJ, Phase DM, Kumar R, et al. Structural, optical and electronic structure studies of Al doped ZnO thin films. *Superlattices and Microstructures.* 2015;**83**:431. DOI: 10.1016/j.spmi.2015.03.047
- [51] Devi V, Kumar M, Choudhary RJ, Phase DM, Kumar R, Joshi BC. Band offset studies in pulse laser deposited $\text{Zn}_{1-x}\text{Cd}_x\text{O}/\text{ZnO}$ hetero-junction. *Journal of Applied Physics.* 2015;**117**:225305. DOI: 10.1063/1.4922425
- [52] Devi V, Kumar M, Kumar R, Singh A, Joshi BC. Band offset measurements in $\text{Zn}_{1-x}\text{Sb}_x\text{O}/\text{ZnO}$ hetero-junctions. *J. Phys. D-Appl. Phys.* 2015;**48**:335103. DOI: 10.1088/0022-3727/48/33/335103
- [53] Devi V, Pandey H, Tripathi D, Kumar M, Joshi BC. Optical and electrical properties of pristine and Al doped ZnO thin films. *AIP Conf. Proc.* 2019;**2136**:040010. DOI: 10.1063/1.5120924
- [54] Devi V, Kumar M, Choudhary RJ, Joshi BC. Structural and optical properties of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ thin films. *AIP Conf. Proc.* 2015;**1661**:110006. DOI: 10.1063/1.4915451
- [55] Bhardwaj R, Kaur B, Singh JP, Kumar M, Lee HH, Kumar P, et al. Role of low energy transition metal ions in Interface formation in ZnO thin films and their effect on magnetic properties for Spintronics applications. *Applied Surface Science.* 2019;**479**:1021. DOI: 10.1016/j.apsusc.2019.02.107
- [56] Kumar M, Singh JP, Chae KH, Lee HH. Structural and electronic properties of ZnO and Ti/Mn:ZnO flexible thin films. *Journal of the Korean Physical Society.* 2020;**77**:452. DOI: 10.3938/jkps.77.452
- [57] Singh JP, Kumar M, Lim WC, Lee HH, Lee YM, Lee S, et al. MgO thin film growth on Si(001) by radio-frequency sputtering method. *Journal of Nanoscience and Nanotechnology.* 2020;**20**:7555. DOI: 10.1166/jnn.2020.18613
- [58] Kumar M, Singh JP, Chae KH, Kim JH, Lee HH. Structure, optical and electronic structure studies of Ti:ZnO thin films. *J. Alloy. Compd.* 2018;**759**:8. DOI: 10.1016/j.jallcom.2018.04.338
- [59] Singh JP, Ji MJ, Kumar M, Lee IJ, Chae KH. Unveiling the nature of adsorbed species onto the surface of MgO thin films during prolonged annealing. *J. Alloy. Compd.* 2018;**748**:355. DOI: 10.1016/j.jallcom.2018.02.344
- [60] Lee S, Ivanov IN, Keum JK, Lee HN. Epitaxial stabilization and phase instability of VO_2 polymorphs. *Scientific Reports.* 2016;**6**:19621. DOI: 10.1038/srep19621
- [61] Choi S, Chang SJ, Oh J, Jang HJ, Lee S. Electrical and optical properties of VO_2 polymorphic films grown Epitaxially on Y-stabilized ZrO_2 . *Adv.*

Electron. Mater. 2018;**4**:1700620. DOI: 10.1002/aelm.201700620

[62] Chamberland BL. New defect vanadium dioxide phases. *Journal of Solid State Chemistry*. 1973;**7**:377. DOI: 10.1016/0022-4596(73)90166-7

[63] Ghedira M, Vincent H, Marezio M, Launay JC. Structural aspects of the metal-insulator transitions in VO_{0.985}Al_{0.015}O₂. *Journal of Solid State Chemistry*. 1977;**22**:423. DOI: 10.1016/0022-4596(77)90020-2

[64] Basu R, Srihari V, Sardar M, Srivastava SK, Bera S, Dhara S. Probing phase transition in VO₂ with the novel observation of low-frequency collective spin excitation. *Scientific Reports*. 2020;**10**:1977. DOI: 10.1038/s41598-020-58813-x

[65] Yang TH, Aggarwal R, Gupta A, Zhou H, Narayan RJ, Narayan J. Semiconductor-metal transition characteristics of VO₂ thin films grown on c- and r-sapphire substrates. *Journal of Applied Physics*. 2010;**107**:053514. DOI: 10.1063/1.3327241

[66] Wong FJ, Zhou Y, Ramanathan S. Epitaxial variants of VO₂ thin films on complex oxide single crystal substrates with 3m surface symmetry. *Journal of Crystal Growth*. 2013;**364**:74. DOI: 10.1016/j.jcrysgro.2012.11.054

[67] Zhang H, Zhang L, Mukherjee D, Zheng Y, Haislmaier R, Alem N, et al. Wafer-scale growth of VO₂ thin films using a combinatorial approach. *Nature Communications*. 2015;**6**:8475. DOI: 10.1038/ncomms9475

[68] Shao Z, Wang L, Chang T, Xu F, Sun G, Jin P, et al. Controllable phase-transition temperature upon strain release in VO₂/MgF₂ epitaxial films. *Journal of Applied Physics*. 2020;**128**:045303. DOI: 10.1063/5.0011423

[69] Kumar M, Rani S, Singh JP, Chae KW, Kim Y, Park J, et al. Structural phase control and thermochromic modulation of VO₂ thin films by post thermal annealing. *Applied Surface Science*. 2020;**529**:147093. DOI: 10.1016/j.apsusc.2020.147093

[70] Wong FJ, Ramanathan S. Synthesis of epitaxial rutile-type VO₂ and VO₂ (B) polymorph films. *Proc. of SPIE*. 2014;**8987**:89870W. DOI: 10.1117/12.2044055

[71] Fan LL, Chen S, Luo ZL, Liu QH, Wu YF, Song L, et al. Strain dynamics of ultrathin VO₂ film grown on TiO₂ (001) and the associated phase transition modulation. *Nano Letters*. 2014;**14**:4036. DOI: 10.1021/nl501480f

[72] Zhao Y, Karaoglan-Bebek G, Pan X, Holtz M, Bernussi AA, Fan Z. Hydrogen-doping stabilized metallic VO₂ (R) thin films and their application to suppress Fabry-Perot resonances in the terahertz regime. *Applied Physics Letters*. 2014;**104**:241901. DOI: 10.1063/1.4884077

[73] Liang YG, Lee S, Yu HS, Zhang HR, Liang YJ, Zavalij PY, et al. Tuning the hysteresis of a metal-insulator transition via lattice compatibility. *Nature Communications*. 2020;**11**:3539. DOI: 10.1038/s41467-020-17351-w

[74] Yoon H, Choi M, Lim T, Kwon H, Ihm K, Kim J, et al. Reversible phase modulation and hydrogen storage in multivalent VO₂ epitaxial thin films. *Nature Materials*. 2016;**15**:1113. DOI: 10.1038/nmat4692

[75] Lee D, Kim H, Kim JW, Lee IJ, Kim Y, Yun H, et al. Hydrogen incorporation induced the octahedral symmetry variation in VO₂ films. *Applied Surface Science*. 2017;**396**:36. DOI: 10.1016/j.apsusc.2016.11.047

[76] Jeong J, Aetukuri N, Graf T, Schladt TD, Samant MG, Parkin SSP.

- Suppression of metal-insulator transition in VO₂ by electric field-induced oxygen vacancy formation. *Science*. 2013;**339**:1402. DOI: 10.1126/science.1230512
- [77] Okimura K, Watanabe T, Sakai J. Stress-induced VO₂ films with M₂ monoclinic phase stable at room temperature grown by inductively coupled plasma-assisted reactive sputtering. *Journal of Applied Physics*. 2012;**111**:073514. DOI: 10.1063/1.3700210
- [78] Ji Y, Zhang Y, Gao M, Yuan Z, Xia Y, Jin C, et al. Role of microstructures on the M1-M2 phase transition in epitaxial VO₂ thin films. *Scientific Reports*. 2014;**4**:4854. DOI: 10.1038/srep04854
- [79] Azhan NH, Su K, Okimura K, Zaghrioui M, Sakai J. Appearance of large crystalline domains in VO₂ films grown on sapphire (001) and their phase transition characteristics. *Journal of Applied Physics*. 2015;**117**:245314. DOI: 10.1063/1.4923223
- [80] Sharma Y, Holt MV, Laanait N, Gao X, Ivanov IN, Collins L, et al. Competing phases in epitaxial vanadium dioxide at nanoscale. *APL Materials*. 2019;**7**:081127. DOI: 10.1063/1.5115784
- [81] Pouget JP, Launois H, D'Haenens JP, Merenda P, Rice TM. Electron localization induced by uniaxial stress in pure VO₂. *Physical Review Letters*. 1975;**35**:873. DOI: 10.1103/PhysRevLett.35.873
- [82] Li W, Dahn JR, Wainwright DS. Rechargeable lithium batteries with aqueous electrolytes. *Science*. 1994;**264**:1115. DOI: 10.1126/science.264.5162.1115
- [83] Lee S, Sun XG, Lubimtsev AA, Gao X, Ganesh P, Ward TZ, et al. Persistent electrochemical performance in epitaxial VO₂ (B). *Nano Letters*. 2017;**17**:2229. DOI: 10.1021/acs.nanolett.6b04831
- [84] Xia C, Lin Z, Zhou Y, Zhao C, Liang H, Rozier P, et al. Large intercalation Pseudocapacitance in 2D VO₂(B): Breaking through the kinetic barrier. *Adv. Mat.* 2018;**30**:1803594. DOI: 10.1002/adma.201803594
- [85] Oka Y, Sato S, Yao T, Yamamoto N. Crystal structures and transition mechanism of VO₂ (a). *Journal of Solid State Chemistry*. 1998;**141**:594. DOI: 10.1006/jssc.1998.8025
- [86] Zhang S, Shang B, Yang J, Yan W, Wei S, Xie Y. From VO₂ (B) to VO₂ (a) nanobelts: First hydrothermal transformation, spectroscopic study and first principles calculation. *Physical Chemistry Chemical Physics*. 2011;**13**:15873. DOI: 10.1039/C1CP20838A
- [87] Chen A, Bi Z, Zhang W, Jian J, Jia QX, Wang H. Textured metastable VO₂ (B) thin films on SrTiO₃ substrates with significantly enhanced conductivity. *Applied Physics Letters*. 2014;**104**:071909. DOI: 10.1063/1.4865898
- [88] Choi S, Ahn G, Moon SJ, Lee S. Tunable resistivity of correlated VO₂(A) and VO₂(B) via tungsten doping. *Scientific Reports*. 2020;**10**:9721. DOI: 10.1038/s41598-020-66439-2